A New Method of the Colorimetric Determination of Small Amounts of Manganese with Silver Peroxide*

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Introduction. Small amounts of manganese can be determined accurately and quickly by the colorimetric method based upon the ease

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with which the manganese solution is oxidized to permanganate. Several oxidizing agents were proposed for this purpose by many workers. At first, lead peroxide was proposed for this purpose by Crum,(1) then sodium bismuthate was introduced by Reddrop and Ramage,(2) ammonium persulfate was tried in the presence of silver ion acting as catalyst by Marshall,(3) alkali periodate was recommended by Willard and Greathouse(4) and nickel dioxide was used by Lang.(5)

It is well known that the excess lead dioxide or sodium bismuthate is defective in that the excess of the reagent must be removed before the comparison can be made. In the application of persulfate, it is sometimes difficult to obtain correct results (4) (6), owing to the difficulty of complete oxidation. As some workers have recommended, the periodate method seems to be the best in overcoming these defects; however, it too has its handicap as it is exceedingly difficult to obtain a good quality and it is also too expensive for the routine work.(7)

In the persulfate method the amount of silver nitrate added is too large to consider its action simply as a catalyst. Therefore Barbier(8) has proposed such an intermediate compound as $3Ag_2O_2 \cdot AgNO_3$ for the process of oxidation, while on the other hand Pinkus(9) suggested the formation of silver peroxide. Although some investigators have studied this problem, none of them have been able to draw any definite conclusion.

The purpose of this investigation was therefore as follows: a) to isolate a silver compound with strong oxidizing power, b) to improve the colorimetric determination of manganese by the application of that compound.

Preparation of Silver Peroxide. On cautiously adding a slight excess of ammonium persulfate to a 10 per cent solution of silver nitrate, stirring constantly, a heavy gray precipitate is soon separated and the supernatant liquid is tinted brown. This gray precipitate is considered to be a mixture of silver peroxide and silver persulfate and the brown liquid is a nitric acid solution of silver peroxide from which silver peroxide can be precipitated when it is diluted. It is washed several times by decantation and transfered to an amber glass stoppered bottle with some water. It is desirable that this be kept in a dark cold place.

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(1) W. Crum, *Lieb. Ann.*, **55** (1845), 219; R. Wasmuth, *Ang. Chem.*, **42** (1929), 133.

(2) J. Reddrop and H. Ramage, *Trans. Chem. Soc.*, **67** (1895), 268; R. O. Gortner and C. O. Rost, *Ind. Eng. Chem.*, **4** (1912), 522.

(3) H. Marshall, *Chem. News*, **83** (1901), 76; M. Dittrich, *Z. anorg. allgem. Chem.*, **80** (1913), 171; R. Lang and F. Kurtz, *Z. Anal. Chem.*, **85** (1931), 181.

(4) H. H. Willard, and L. H. Greathouse, *J. Am. Chem. Soc.*, **39** (1917), 2366.

(5) R. Lang, *Z. anorg. Chem.*, **158** (1926), 370.

(6) R. O. Gortner and C. O. Rost, *Ind. Eng. Chem.*, **4** (1912), 522.

(7) H. H. Willard and J. J. Thompson, *Ind. Eng. Chem., Anal. Ed.*, **3** (1931), 399; G. J. Hough, *Ind. Eng. Chem., Anal. Ed.*, **7** (1935), 408.

(8) G. A. Barbier, *Ber.*, **60** (1927), 2424; A. Travers, *Compt. rend.*, **182** (1926), 972.

(9) A. Pinkus and L. Ramakers, *Chem. Zentr.*, **1** (1933), 1658; *Bull. Soc. Chem. Belgium*, **41** (1933), 529.

The precipitate thus obtained will be employed as a new energetic oxidizing agent and, for the sake of convenience, is called silver peroxide hereafter though it may be a mixture as mentioned above. A freshly precipitated silver peroxide may on standing undergo a change in contact with water forming a darker precipitate. It is supposed that the following reaction takes place⁽¹⁰⁾: $Ag_2S_2O_8+2H_2O\rightarrow Ag_2O_2+2H_2SO_4$

When silver peroxide is added to the solution containing manganese acidified with sulfuric acid it is decomposed in a little while in the following way: $Ag_2O_2+H_2SO_4 \rightarrow Ag_2SO_4+H_2O+O$

In this case the silver sulfate thus formed is a strong catalyst which decomposes hydrogen peroxide and liberates oxygen in the nascent state in the acid solution.

The oxidizing power of silver peroxide is retained for approximately half a year or more without any decrease in power as shown in Table 1.

Table 1. Oxidizing power and the duration after preparation.

Duration after preparation (days)	1	7	14	21	28	67	148
MnO found (γ)	104.1	104.2	104.0	104.1	104 1	103.9	104.2

The tested solution contains 140.0 γ MnO in 25 c.c. solution acidified with sulfuric acid.

Outline of Method.

A stock solution of manganese sulfate containing 0.1g. of MnO per liter is prepared by reducing potassium permanganate solution in the usual way. The standard solution of manganese containing 104.0 γ of MnO used in this investigation was obtained by suitably diluting the above stock solution.

The addition of silver peroxide (name given the precipitate as aforementioned) to the acidified solution containing manganese, at room temperature and with stirring, instantaneously produces the maximum coloration due to the formation of permanganate ion. Any excess of the reagent which is left suspending in the solution is easily decomposed by warming on a water bath for 2 to 3 minutes after which the solution will be left clear. The relation between the time and temperature required for the decomposition is shown in Table 2. Though the duration after the reagent has been prepared does not reduce its oxidizing power it has been found that decomposition of excess reagent becomes quicker by long standing.

Table 2. Time required for complete decomposition at various temperatures.

°C / days	92.5	70	60	50	40	20	10
2	3 min.	9 min.	13 min.	24 min.	45 min.	— min.	— min.
13	2	—	3	—	6	10	—
21	2	—	2	—	3	—	8

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(10) Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," vol. III. p. 383, New York (1929): W. Machu, "Das Wasserstoff Peroxide und die Perverbindungen," S. 236, Wien (1937),

Through this experiment the Pulfrich photometer with filter S53 (maximum absorption 530 mμ) was used. As previous workers have reported, it was found that the Lambert-Beer's law holds closely in this method.

(a) **Concentration of sulfuric acid.** The oxidation is carried out at various concentrations as shown in Table 3. Best results were obtained by using 8 to 12 per cent sulfuric acid solution. In the following experiments, a 10 per cent solution was used with a few exceptions.

Table 3. Suitable concentration of sulfuric acid.

Concentration of $H_2S\ O_4$ (%)	MnO found (γ)		% of coloration*	
1	82.7	84.0	79.5	80.7
5	98.2	96.7	94.4	93.0
8	104.0	103.4	100.0	99.4
12	103.7	104.3	99.7	100.3
25	103.4	103.1	99.4	99.2
30	97.8	96.3	94.0	92.8

* % of coloration is calculated from MnO (found)/MnO (calculated). In the above MnO (calculated) is 104.0 γ.

(b) **Quantity of oxidizing agent.** It is convenient to handle about 0.1 to 0.15 g. (call this one unit). About 100 γ MnO is oxidized sufficiently by one unit as shown in Table 4. Only two units of silver peroxide is sufficient to oxidize about 800 γ manganese as MnO. If the MnO concentration is more than 10 p. p. m., the violet precipitate, presumably siver permanganate, is formed. It is, therefore, preferable to use the sample solution containing less than 10 p. p. m. of manganese as MnO.

Table 4. Amounts of silver peroxide necessary for oxidation of manganese.

Quantity (unit)	1/2		1		15		15	
MnO found (γ)	90.5	93.4	104.3	103.7	104.3	104.1	104.0	104.3
Difference (γ)	−13.5	−10.6	+0.3	−0.3	+0.3	+0.1	0	+0.3

The test solution contains 104.0 γ manganese as MnO in 25 c.c.

(c) **Removal of excess silver peroxide.** The addition of the reagent darkens the solution. However this excess can be removed only by warming it on a water bath or by letting the solution stand for several minutes as described already. The reagent should not in any case be added to a hot solution as oxidation will no doubt be insufficient. Maximum coloration is obtained by a 2 minutes heating. Undue prolonged heating reduces the coloration.

Table 5. Differences due to heating time.

Heating time (min.)	2	4	5	7	10
MnO found (γ)	104.0	103.6	102.5	97.0	77.3
Difference (γ)	0	−0.4	−1.5	−7.0	−26.7

The test solution contains 104.0 γ manganese as MnO in 25 c.c.

(d) **Standard curve and accuracy.** Oxidation of the various concentrations of manganese is performed in strict adherence to the condition as already established. The extinction coefficient of permanganate solution thus obtained was measured with the results shown in Table 6.

Table 6. Extinction coefficients of the solutions after oxidation of manganese by silver peroxide.

Manganese as MnO in p. p. m.	2.80	4.16	6.24	8.32
No. 1 (av. of eight readings)	0.2002	0.4039	0.6043	0.8048
No. 2 (av. of eight readings)	0.2009	0.4028	0.6034	0.8057
No. 3 (av. of eight readings)	0.2008	0.4013	0.6052	0.8059
No. 4 (av. of eight readings)	0.2018	0.4041	0.6044	0.8049
No. 5 (av. of eight readings)	0.2022	0.4017	0.6043	0.8056
Average	0.2012	0.4028	0.6037	0.8052

Filter: S53, length of the cell: 30.04 mm.

From these data the following relation between concentration and extinction coefficient is calculated by the application of least squares where X is the concentration of manganese as MnO in p. p. m. and E, the extinction coefficient of the length of 10.00 mm. cell used.

$$X = 3.439\ E$$

To make sure of this relation, the extinction coefficient of permanganate solution having the same acidity was measured at various concentrations as shown in Table 7 (A). The same relation was obtained.

$$X = 3.435\ E$$

It was found that results obtained by this proposed method coincide with the true value allowing for minimum difference. In other words, the accuracy of this method is proved to be satisfactory.

For purpose of comparison the potassium permanganate is treated in the same way as mentioned above (see Table 7 (B)). The following equation was obtained in the same way from the results which were cited in Table 7 (B).

$$X = 3.439\ E$$

Table 7. Extinction coefficients of potassium permanganate solution when oxidation is done (B) or not (A).

E	A				B			
MnO p. p. m. / Exp.	No. 1	No. 2	No. 3	Ave.	No. 1	No. 2	No. 3	Ave.
1.992	0.1938	0.1935	0.1922	0.1932	0.1929	0.1931	0.1918	0.1926
3.984	0.3868	0.3860	0.3851	0.3859	0.3864	0.3859	0.3852	0.3858
5.976	0.5799	0.5780	0.5807	0.5795	0.5787	0.5793	0.5779	0.5786
7.968	0.7733	0.7720	0.7716	0.7723	0.7728	0.7710	0.7714	0.7717

E: Average of eight readings in one determination. Filter: S53, the length of the cell: 30.04 mm.

The results obtained correspond with the true value thus proving that silver peroxide has no obstructive effects on the process of oxidation. Thus it can be concluded from these results that silver peroxide is a superior oxidizing agent.

(e) **Reproducibility.** The following experiments were carried out to certify the accuracy of this method at various concentrations of manganese.

Table 8. Reproducibility of this method.

MnO present	MnO found (γ)					E	
						min.	max.
104.0 γ in 50 c.c.	103.4	103.8	103.7	104.3	104.5	0.2002	0.2022
104.0 γ in 25 c.c.	104.3	104.0	103.7	104.4	103.7	0.4013	0.4041
208.0 γ in 25 c.c.	207.9	208.1	208.2	207.9	208.1	0.8048	0.8059
312.0 γ in 50 c.c.	312.2	311.8	312.7	312.3	312.2	0.6034	0.6052
832.0 γ in 200 c.c.	828.5	830.4	829.5	832.2	831.0	0.4009	0.4027

E: Average of eight readings in one determination. Silver oxide: 2 units, acid concentration: 8%. Filter: S53, the length of the cell: 30.04 mm.

Thus it was proved that the proposed method may be used satisfactorily as a quick and accurate colorimetric method. Whatever difference may be caused it will be limited to 1.5 per cent.

(f) **Interference of various ions.** It is necessary to study the interference of various ions as the oxidizing agent used herr has been newly tried.

The interference ions are divided into three groups: 1) colorless ions, 2) colored ions, 3) ions precipitated by silver, sulfate ions or in acid solution.

(1) Colorless ions. Some colorless ions do not interfere with the colorimetric determination of manganese as would be expected. As a large quantity of ferric ion interferes with the coloration of the permanganate, the addition of phosphoric acid is necessary to prevent this interference. Some reducing ions, namely ferrous, sulfite, nitrite, oxalate, tartrate and other oxidizable organic anions in small amounts can be easily oxidized with further addition of silver peroxide. White silver sulfate will sometimes precipitate. In this case it is desirable to reoxidize after filtering off. If a large amount of such ions is present, it is safer to remove or destroy the ions by evaporation with nitric acid or a mixture of nitric acid and sulfuric acid before the oxidation is carried out. (see Table 9).

(2) Colored ions. Some interferences are expected when the colored ions are present in the sample solution. However the effect of some of these may be compensated by the use of an aliquot portion or by the addition of the same amount in the reference cell of photometer as shown in Table 10.

As the above tests have indicated there is no obstacle met by the presence of these ions especially chromium, titanium, up to the above concentration in the application of this new reagent. None of these interferences need be considered because the cited ions can be easily separated by the usual method.

(3) Ions precipitated by silver ion, sulfate ion or in acid solution. Chloride precipitates by a slight excess of silver nitrate. However it is preferable to remove it by evaporation with sulfuric acid. Other ions may be removed simply by filtration with no serious effects as shown in Table 11.

Proposed Method. As already described it is proved that the colorimetric determination of manganese may be successfully performed by utilizing the new oxidizing agent. The general procedure will be des-

Table 9. Ions which have no interfering effect.

Ions	Salt used	Amount present (against 104.0 γ MnO) (mg.)	MnO found (γ)	Difference (γ)
Al^{+++}	$Al_2(SO_4)_3$	Al 100 (1:1000)	103.8	—0.2
As^{+++}	As_2O_3	As_2O_3 100 (1:100)	103.8	—0.2
NH_4^+	$(NH_4)_2SO_4$	NH_4 100 (1:1000)	103.8	-0.2
Bi^{+++}	$Bi(NO_3)_3$	Bi 10 (1:100)	104.0	0
Ca^{++}	$Ca(NO_3)_2$	Ca 10 (1:100)	104.0	0
Cd^{++}	$Cd(NO_3)_2$	Cd 100 (1:1000)	103.6	-0.4
Fe^{+++}	$Fe(NO_3)_2$	Fe 100 (1:1000)	104.0	0
Mg^{++}	$MgSO_4$	Mg 100 (1:1000)	103.4	—0.6
Sn^{++++}	$Sn(SO_2)_4$	Sn 100 (1:1000)	103.9	-0.1
Tl^+	Tl_2SO_4	Tl 10 (1:100)	103.3	—0.7
Zn^{++}	$ZnSO_4$	Zn 100 (1:1000)	103.6	-0.4
VO_3^-	NH_4VO_3	V_2O_3 10 (1:100)	104.2	+0.2
BO_2^-	$Na_2B_4O_7$	B_2O_3 100 (1:1000)	103.7	—0.3
MoO_4^{--}	$(NH_4)_6Mo_7O_{24}4H_2O$	MoO_3 140 (1:1400)	104.2	+0.2
PO_4^{---}	Na_2HPO_4	P_2O_5 1000 (1:10000)	104.0	0
SiO_3^{--}	Na_2SiO_3	SiO_2 5 (1:50)	104.1	+0.1
F^-	NaF	F 0.16 (1:1.6)	104.0	0
NO_3^-	HNO_3	NO_3 2.8 (1:28000)	104.0	0
PO_4^{---}	H_3PO_4	P_2O_5 1500 (1:15000)	104.4	+0.4
$C_2O_4^{--}$	$(COONa)_2$	C_2O_4 14 (1:140)	104.2	+0.2
$C_4H_4O_6^{--}$	$NaKC_4H_4O_6$	$C_4H_4O_6$ 5 (1:50)	103.8	-0.2

Table 10. Colored ions.

Ions	Salt used	Amount present (against 104.0γ) (mg.)	MnO found (γ)	Difference. (γ)	Remarks
Cr^{+++}	Chrom-alum	Cr 10 (1:100)	103.2	—0.8	after oxidation with Na_2O_2
$Cr_2O_7^{--}$	K_2CrO_4	Cr 10 (1:100)	104.1	+0.1	
Cu^{++}	$CuSO_4$	Cu 100 (1:1000)	104.2	+0.2	
Cu^{++}	$CuSO_4$	Cu 100 (1:1000)	104.3	+0.3	isolated as CuS
Nd^{+++}	$Nd(NO_3)_3$	Nd_2O_3 50 (1:500)	104.6	+0.6	
Ni^{++}	$NiSO_4$	Ni 50 (1:500)	104.5	+0.5	acid concentration 25 %
Ti^{++++}	$Ti(OH)_4$	TiO_2 10 (1:100)	104.0	0	added 10 units
rare earths	nitrate	about 50 (1:500)	103.8	—0.2	$Nd(NO_3)_3$ containing other rare earths
Co^{++}	$CoSO_4$	Co 10 (1:100)	104.3	+0.3	the comparison solution must be treated as a sample with silver peroxide

cribed below. If the sample contains a large amount of chloride add sulfuric acid and evaporate until fumes of the latter appear. If the amount of chloride is small it may be separated as silver chloride.

Table 11. Ions precipitated in the procedure.

Ions	Salt used	Amount present against 104.0 γ (mg.)	MnO found (γ)	Difference (γ)	Remarks
Ba^{++}	$Ba(NO_3)_2$	Ba 100 (1:1000)	104.6	+0.6	
Sr^{++}	$Sr(NO_3)_2$	Sr 100 (1:1000)	104.0	0	
Hg_2^{++}	$Hg_2(NO_3)_2$	Hg 100 (1:1000)	103.8	−0.2	
Cl^-	NaCl	Cl 100 (1:1000)	103.8	−0,2	
Pb^{++}	$Pb(NO_3)_2$	Pb 100 (1:1000)	104.0	0	
Ca^{++}	$Ca(NO_3)_2$	Ca 100 (1:1000)	103.7	−0.3	alcohol added to decrease the solubility
Ca^{++}	$Ca(NO_3)_2$	Ca 50 (1:500)	104.1	+0.1	isolated as oxalate
SiO_3^{--}	Na_2SiO_3	SiO_2 100 (1:1000)	103.8	−0.2	separated as insoluble SiO_2
SiO_3^{--}	Na_2SiO_3	SiO_2 100 (1:1000)	104.3	+0.3	SiO_2 filtered off after treating with H_2SO_4
WO_4^{--}	Na_2WO_4	W 100 (1:1000)	104.1	+0.1	digested with HNO_3 and filtered

In the presence of a large quantity of ferrous ion and other oxidizable substance, boil with nitric acid or add the later before evaporating with sulfuric acid. The best method for the separation of chromium involves oxidation in basic solution as many workers have recommended, whereby manganese is precipitated with iron, titanium and others. In like manner other undesirable matter can be easily separated from manganese with no interfering effects.

It is most convenient to apply hydroxide precipitation method with a little ferric salt as a collector to concentrate very small amounts of manganese as in the case of natural water (as little as 10 γ per liter). The sample solution thus obtained ready for colorimetric determination should contain 10 per cent of sulfuric acid in the final step. Then add about 0.1 g. silver peroxide stirring constantly. Heat on water bath for 2 minutes or let stand for several minutes to obtain the maximum coloration of the manganese. Dilute to the definite volume and make the color comparison in any convenient way.

By this method as little as 1 p.p.m. of manganese (as MnO) can be easily determined with the best results. This method was retested by determining manganese in natural water, hot springs water and biological materials; results of which will be given in a latter communication.

Summary

In face of several defects noted by the oxidation agents hitherto used in the determination of manganese by the colorimetric method a new reagent, so-called "Silver peroxide," has been proposed. This new reagent

has been found to excel other reagents in the following respects: a) easy preparation and easy decomposition of the excess reagent, b) strong oxidizing power not reduced by long standing and cheap availability for routine work, c) no noticeable interference by other reagents during action and accuracy in results obtained.

Thus by its use the procedure is exceedingly simplified and the time required is considerably less than that in the method used hitherto.

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